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Theoretical studies of nanoclusters

23 Jul 2015

Briefer: Jerry Boatz, Ph.D.
Principal Research Chemist
Aerospace Systems Directorate, RQRP
Air Force Research Laboratory

This briefing contains information up to:

Outline

1. **Introduction**
   - Modeling and simulation methods
     - objectives, payoffs, approach

2. **Aluminum nanoparticles**
   - energetic additives for propellants, explosives
   - “hybrid” fuels consisting of nanoparticles suspended or dissolved in ionic liquids
   - surface-functionalized NPs can be dispersed in variety of liquids hydrocarbons, ILs, polar solvents, etc.

3. **Core-shell nanoclusters**
   - energetic additives for propellants, explosives
   - gas generators
   - biocidal defeat agents

4. **Summary and conclusions**

Objectives

- **Support and streamline the discovery, synthesis, and characterization of new energetic materials for chemical propulsion, explosives, gas generators, etc.**
  - predictions that are accurate, relevant, and timely.
- **Utilize modeling and simulation as computational tool to**
  - identify suitable target compounds
    - "what-if" scenarios, trial-and-error explored via M&S
  - explore possible synthesis routes
  - confirm successful synthesis
  - provide detailed analysis of chemistry & mechanisms
- **Expand scope and complexity of problems which can be addressed via M&S & improve M&S reliability**

Payoffs

- **Focus experimental efforts in the most promising directions**
- **Identify technical “dead ends” early in the propellant development cycle**
- **Provide fundamental insight into observed behavior of materials**
- **Enable rational design approaches in development of advanced materials**

Technical Approach

- **Utilize robust, physics-based M&S**
  - Quantum chemical methods (molecular quantum mechanics)
  - Predictive capability
    - no parameterization, empirical fitting, etc.

- **Leverage fundamental R&D**
  - AFOSR support for computational chemistry
    - e.g., development of “fragment” methods for large-scale computations
  - NRC postdocs, senior fellowships, summer faculty fellowships

- **Leverage DoD HPC resources**
  - ~100M cpu hours / year
  - HPC frontier, HPC HASI, and PETTT pre-planned projects
  - Institutes (e.g., Multi-Scale Reactive Modeling)

Aluminum nanoparticles

- Al nanoparticles (NPs) are of interest as energetic ingredients in explosives and propellant formulations, due to high energy density, enhanced burn rates, etc.

- Efficient production of Al nanoparticles via ball milling is obtained using NH_3, CH_3NH_2, or CH_3CN as milling agents.

- Milling agents decompose on NP surface to produce gaseous products and surface-bound species.

- Milling agents can also passivate NP surface against oxide layer formation

Ball milling gaseous byproducts

Milling agent/ Gaseous products	NH_3	CH_3NH_2	CH_3CN
H_2	√	√	√
CH_3NHCH_3		√	
CH_2NH		√	
CH_4			√
CH_3CH_3			√

Can theory explain, for example in the case of NH_3 as the milling agent, the predominant formation of H_2 as well as the absence of other stable N_xH_y species (N_2, N_2H_2, N_2H_4?)

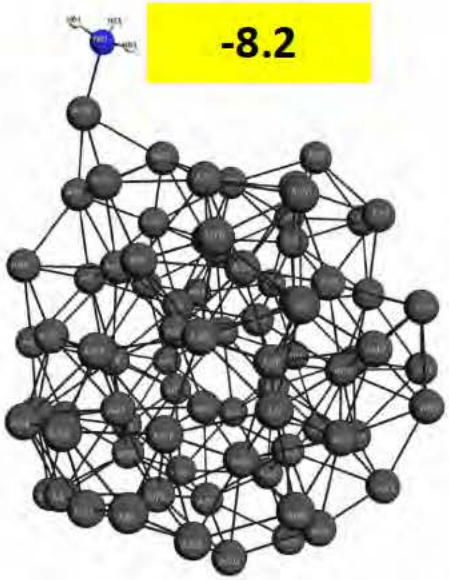
Quantum chemical calculations

- **DFT calculations (M06/6-311++G(d,p)) used to identify surface species and reactions leading to their formation.**

- **Al_{80} nanocluster used as NP model.**
  - contains bulk-like “core” partially surrounded by surface layer
  - surface is atomically “rough” – realistic representation of actual NP surface?

- **Reaction enthalpies and barriers for**
  - chemisorption of NH_3
  - fragmentation of chemisorbed NH_3
  - formation of H_2
    - direct elimination of H_2 from chemisorbed NH_3
    - dissociative recombination of chemisorbed H atoms
    - dissociative elimination of H_2 from adjacent chemisorbed NH_x (x=1-3)
  - formation of N_2, N_2H_2, N_2H_4 (not observed in experiments)

NH_3 chemisorbed on Al_{80}



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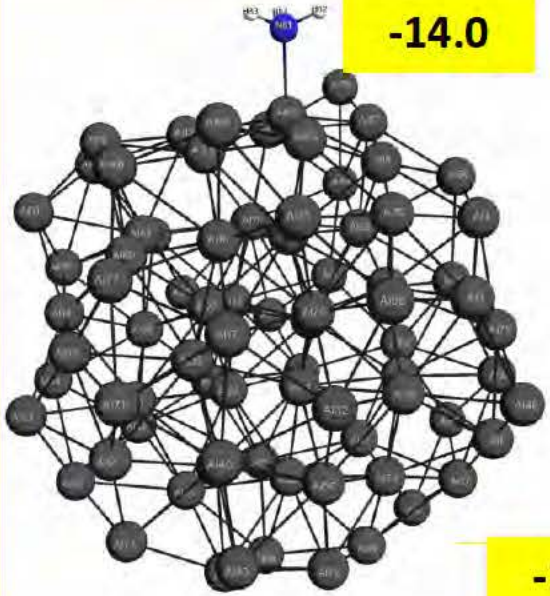

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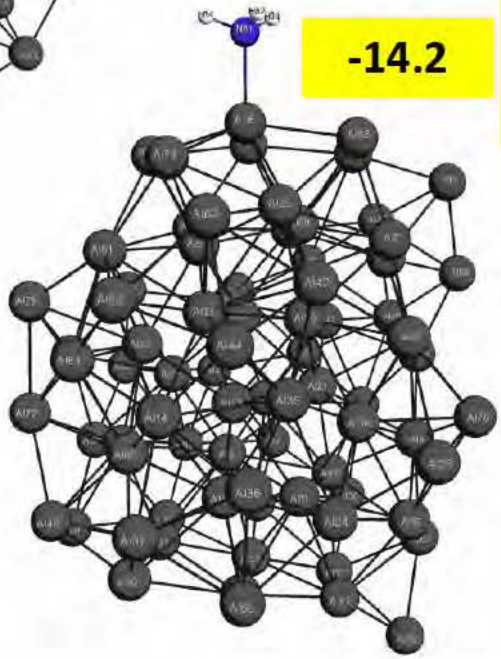

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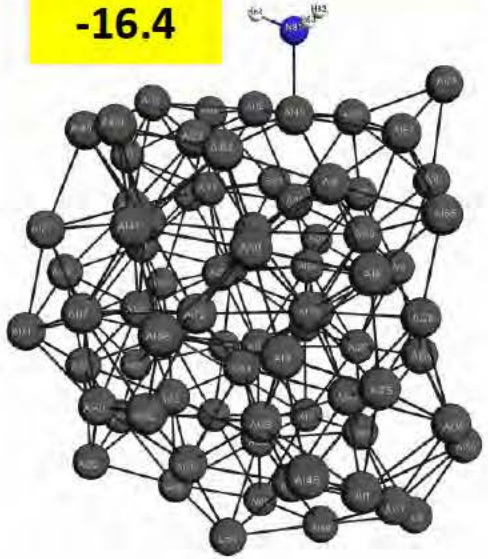

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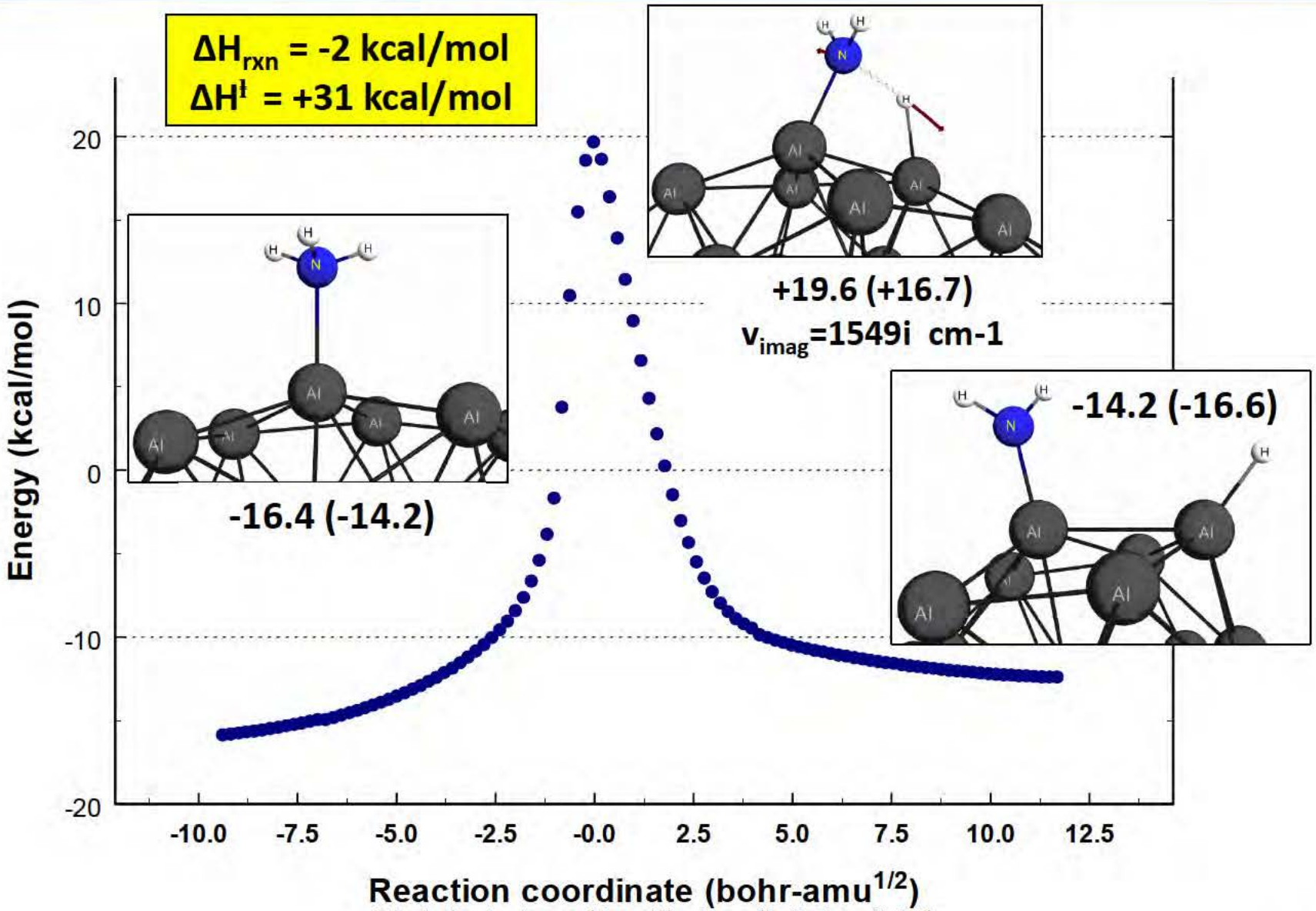
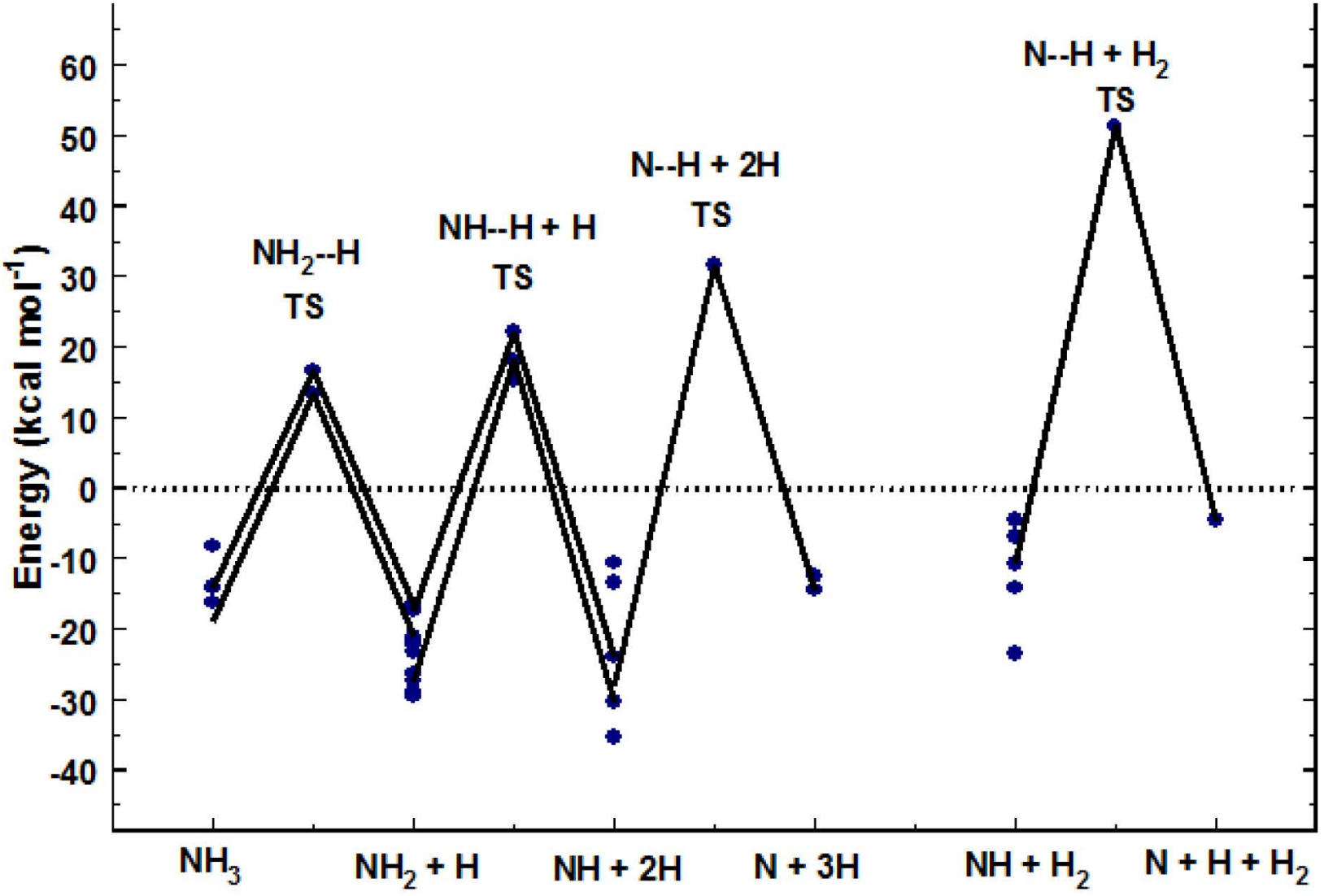
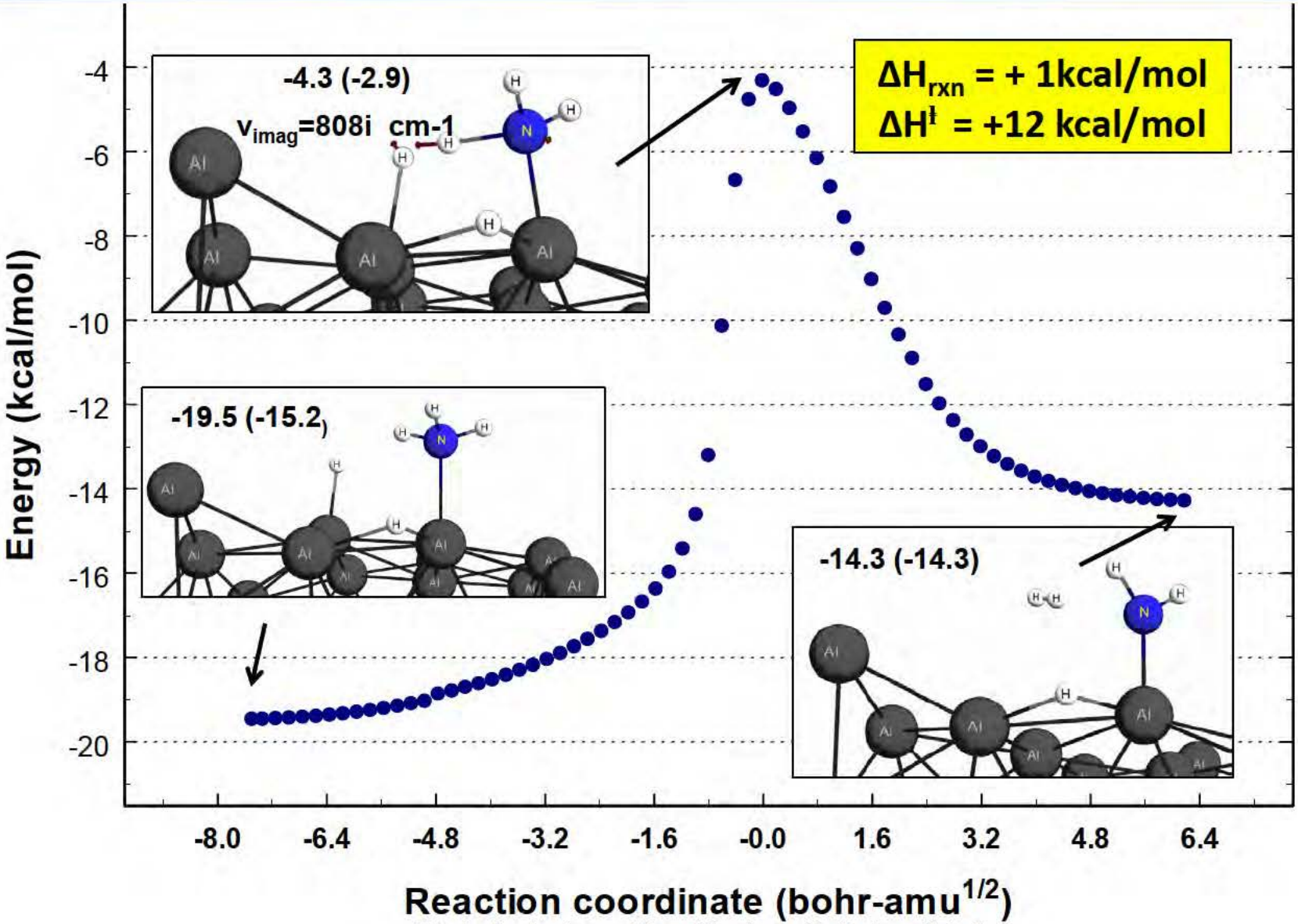
$H_3N{:}Al_{80} \rightarrow NH_2\text{-}Al_{80}\text{-}H$



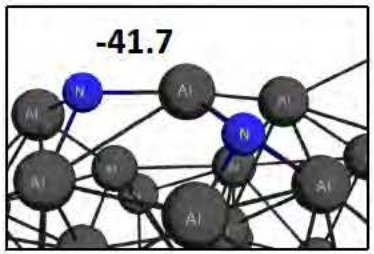
Fragmentation of NH_3 on Al_{80}

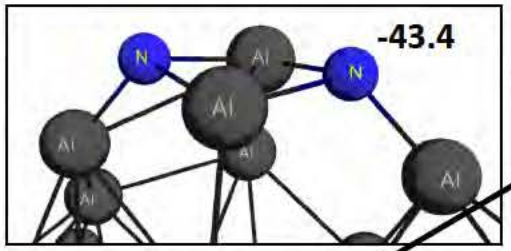


Formation of H_2

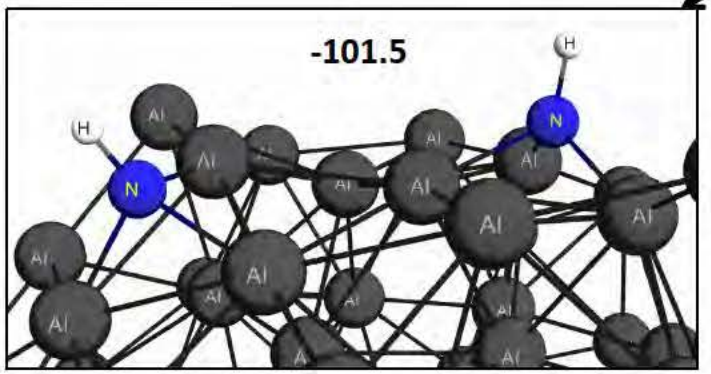


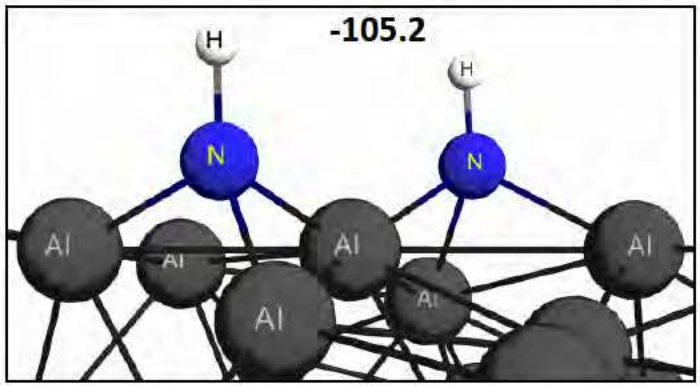
Formation of N_2, N_2H_2, N_2H_4

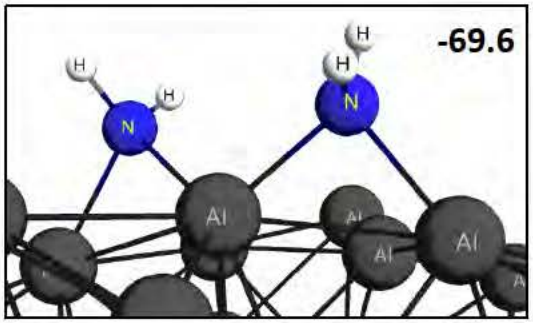


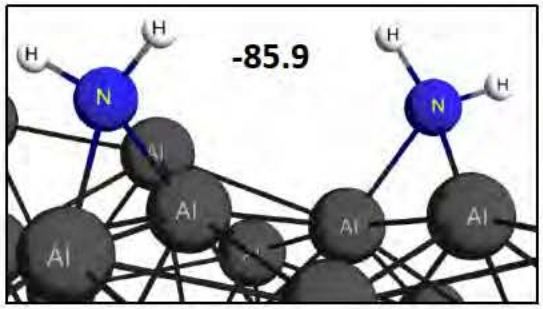


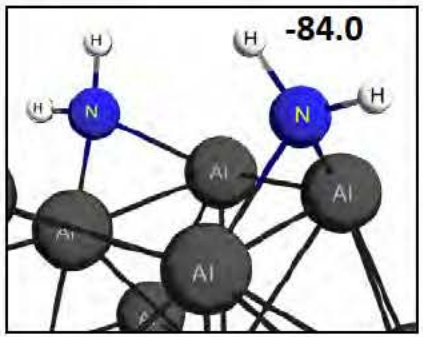
N_2: ΔH_{rxn} = +42-43 kcal/mol
N_2H_2: ΔH_{rxn} = +102-105
N_2H_4: ΔH_{rxn} = +70-90

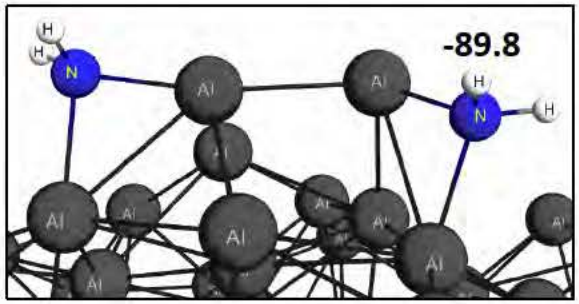










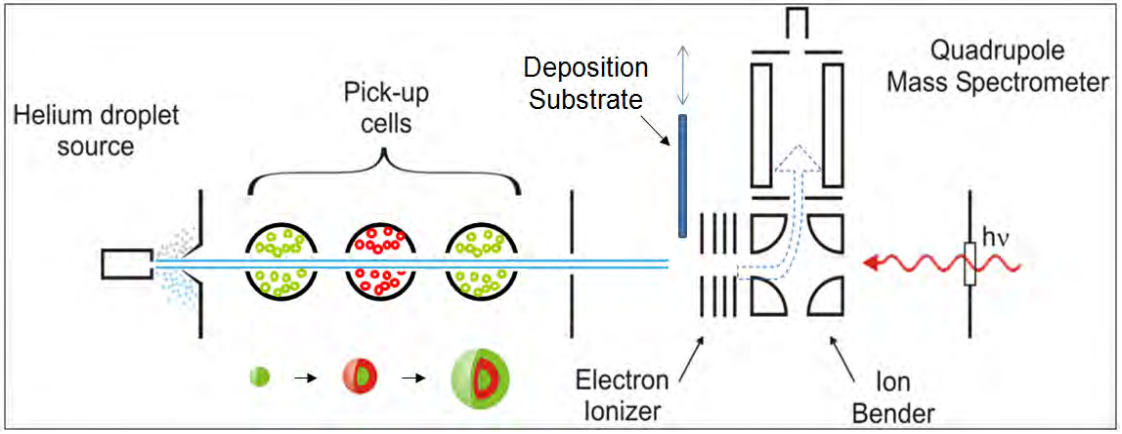


Core-shell nanocluster synthesis

Core-shell nanoclusters such as $SiAl_n$, Ni_nAl_m, $Al_n(CuO)_m$, etc. may be useful ingredients in propellants and explosives

- higher energy densities than organics (~ 3x RDX)

- some are resistant to surface oxidation (i.e., "magic clusters")



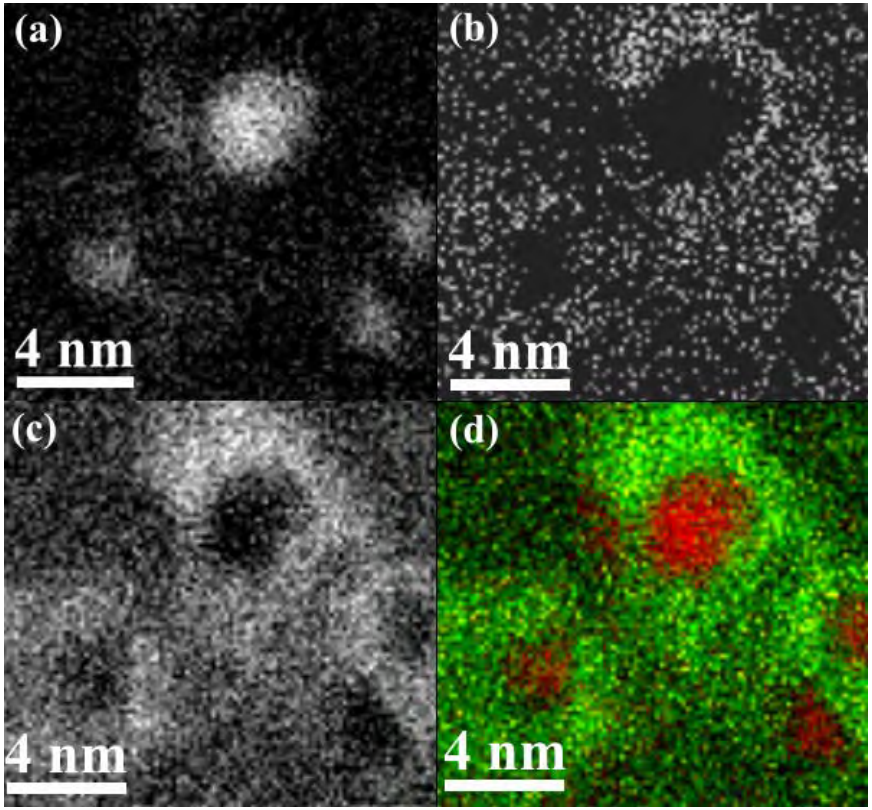
Helium droplet experiments at AFRL/RW

Can core-shell nanoclusters be formed under cryogenic conditions (i.e., in helium droplet experiments) via stepwise condensation; i.e., what are the energy barriers (if any) to stepwise addition of atomic Al?

$SiAl_n + Al \rightarrow SiAl_{n+1}$; $[Al_n]^- + Al \rightarrow [Al]^-$

Cu_xMg_y core-shell nanocluster inversion

In helium droplet experiments, Mg atoms were captured in first pickup cell, followed by capture of Cu atoms to form Cu_xMg_y core-shell nanoclusters. However, scanning transmission electron microscopy (STEM) measures show cluster inversion occurred to produce Mg_yCu_x(!)



a) copper atoms

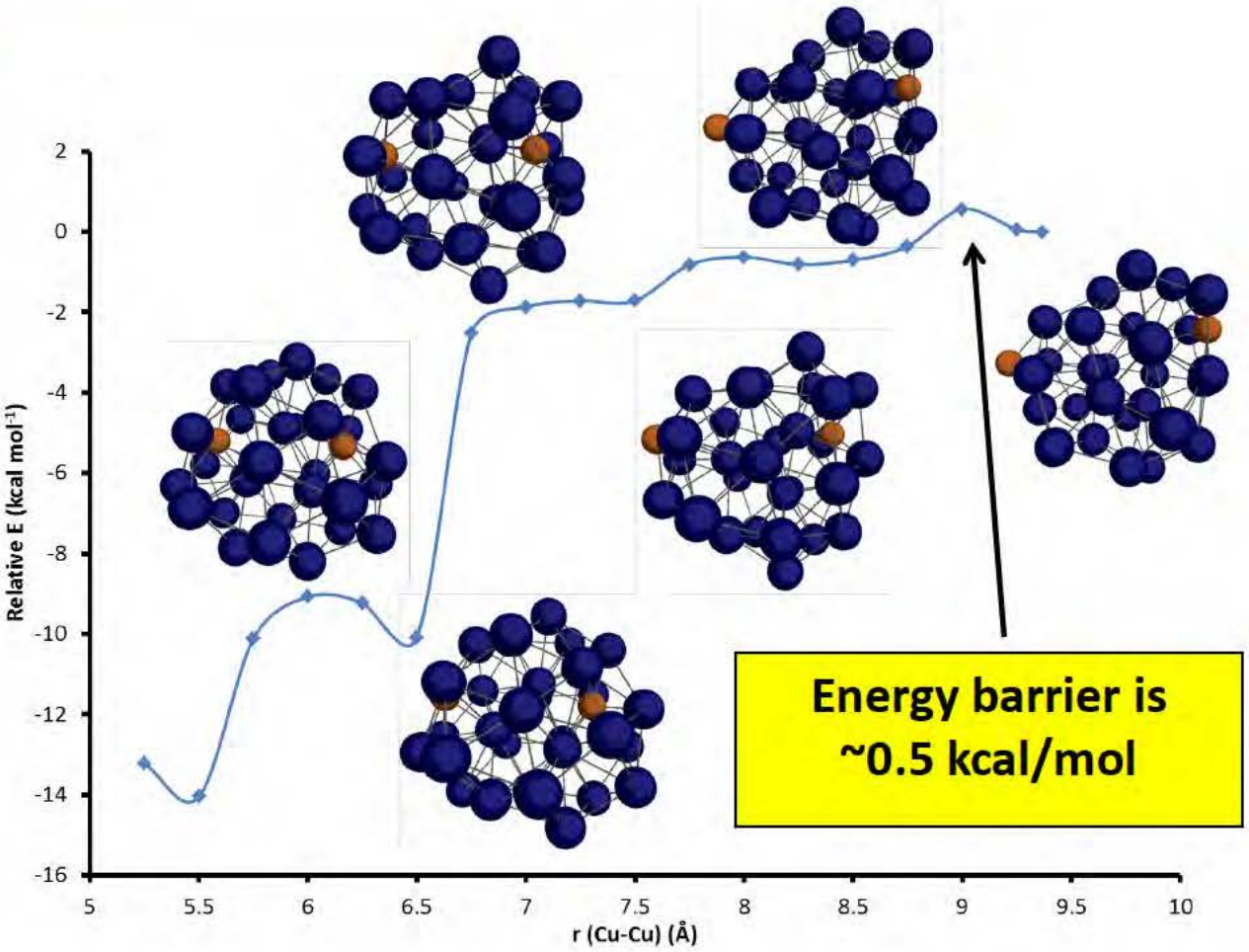
b) magnesium atoms

c) oxygen atoms

d) composite image

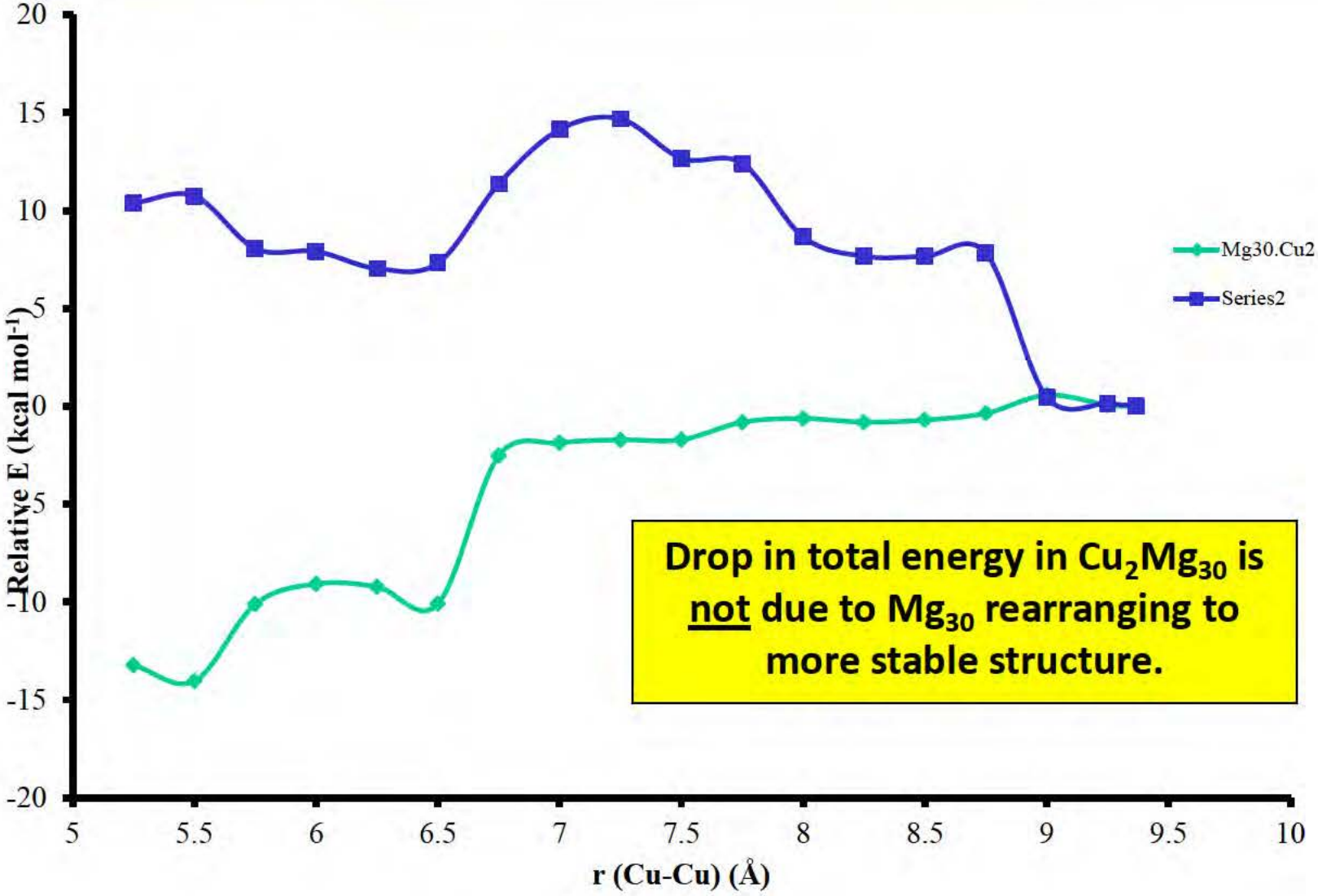
Cu_2Mg_{30}

1. Structure of Mg_{30} cluster was fully optimized.
2. Two Cu atoms were placed on opposite sides of Mg_{30} and structure reoptimized.
3. Distance between Cu atoms was decreased in steps of 0.25 Å, held fixed, and remaining DOF reoptimized.
4. Total energy plotted as function of fixed Cu-Cu distance.

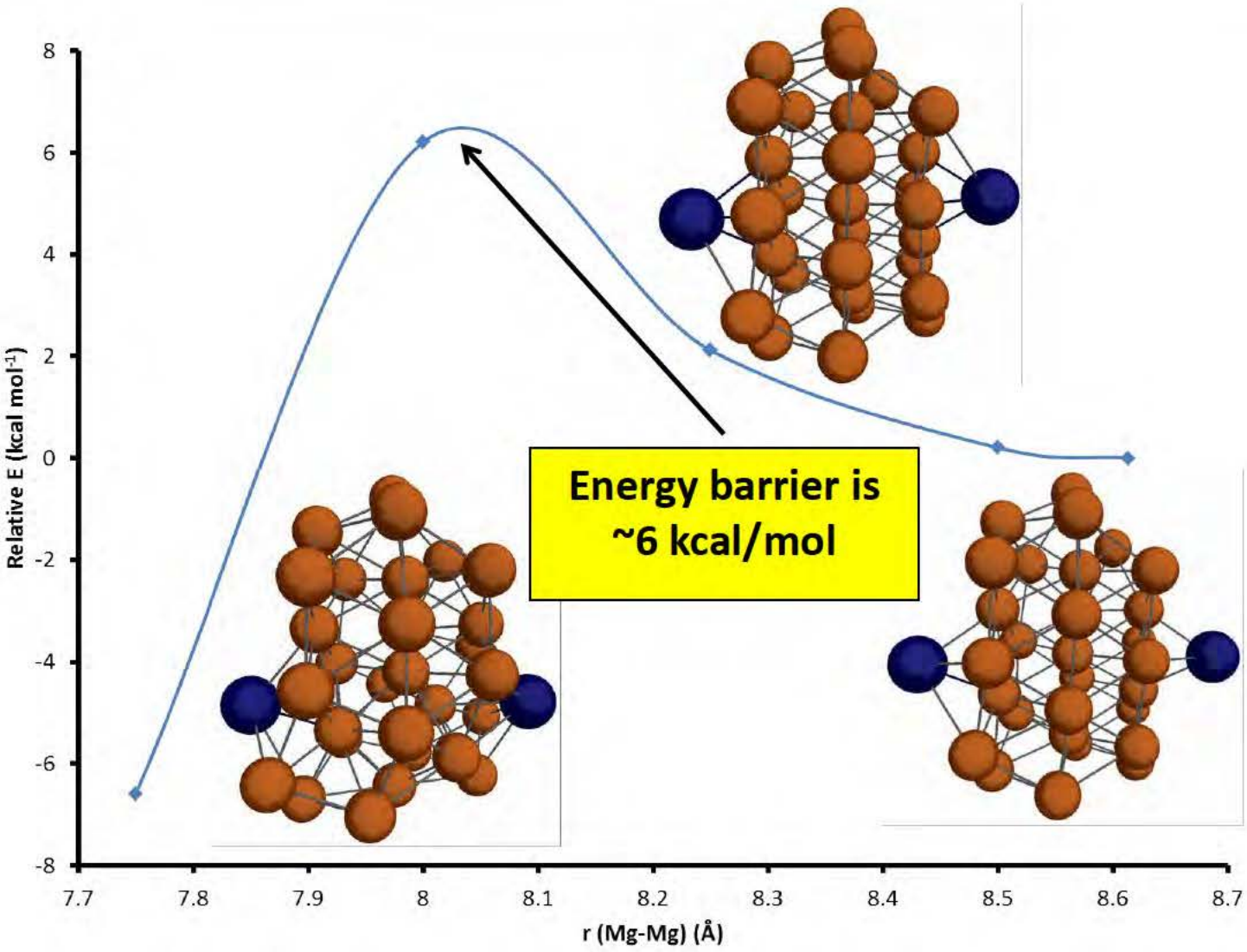


DFT calculations: B3PW91/aug-cc-pωCVTZ(-PP) level

Cu_2Mg_{30} vs. Mg_{30}



$Cu_{30}Mg_2$



Need for HPC

- **Individual job characteristics**

  - Al_{80} + NH_3 (per individual system)
    - Structure optimization: 600 – 1200 cores x 200 hours wall time
      = **120-240K core-hours**
    - Vibrational frequencies: 2500 – 5000 cores x 200 hours wall time
      = **500K-1M core-hours**
    - Intrinsic reaction coordinate: 600-1200 cores x 400 hours wall time
      = **240-480K core-hours**

  - Cu_2Mg_{30}
    - Structure optimization: 2400-3200 cores x 100 hours wall time
      = **240-300K core-hours**
    - Vibrational frequencies: 2400-3200 cores x 300 hours wall time
      = **720-960K core-hours**

Summary and Conclusions

- **Production of Al nanoparticles via ball milling**
  - NH_3-assisted ball milling of Al powder efficiently produces Al NPs, with H_2 as the predominant byproduct.
  - Surface reactions of NH_3 on Al_{80} have been modeled using DFT
    - NH_3 chemisorbs to Al_{80} with binding energies of 8-16 kcal/mol
    - Surface fragmentation of NH_3 to form chemisorbed NH_2 + H is slightly exothermic but has a barrier of 30 kcal/mol.
    - Elimination of H_2 from adjacent chemisorbed H and NH_3 is slightly endothermic but has a barrier of only 12 kcal/mol.
    - Formation of N_2, N_2H_2, N_2H_4 from recombination of chemisorbed N, NH, and NH_2 respectively, is endothermic by ~42, 103, 70 kcal/mol.
  - Calculations are consistent with observation of H_2 as the predominant byproduct and minimal amount of N_2.

- **Mg/Cu core-shell nanoclusters**
  - Helium droplet experiments show inversion of Cu_xMg_y clusters to Mg_yCu_x.
  - Cu atoms diffusing into $Mg_{30,}$ and vice-versa, have been modeled using DFT.
    - Estimated barrier for Cu atoms to migrate into Mg_n is < 1 kcal/mol.
    - Estimated barrier for Mg atoms to migrate into Cu_n is 6 kcal/mol.
  - Calculations are consistent with observed Cu/Mg inversion.

Recent Publications

Parker D. McCrary, Preston A. Beasley, O. Andreea Cojocaru, Stefan Schneider, Tommy W. Hawkins, J. Paulo Perez, Brandon W. McMahon, Mark Pfeil, Jerry A. Boatz, Scott L. Anderson, Steven F. Son, and Robin D. Rogers, "Hypergolic Ionic Liquids to Mill, Suspend, and Ignite Boron Nanoparticles", *Chemical Comm.*, **48**, 4311-4313 (2012).

Parker D. McCrary, Preston A. Beasley, Steven P. Kelley, Stefan Schneider, Jerry A. Boatz, Tommy W. Hawkins, Jesus Paulo L. Perez, Brandon W. McMahon, Mark Pfiel, Steven F. Son, Scott L. Anderson and Robin D. Rogers, "Tuning azolium azolate ionic liquids to promote surface interactions with titanium nanoparticles leading to increased passivation and colloidal stability", *Phys. Chem. Chem. Phys*., **14**,13194-13198 (2012).

Robert J. Buszek, C. Michael Lindsay, and Jerry A. Boatz, "Tetrakis(nitratoxycarbon)methane (née CLL-1) as a potential explosive ingredient: a theoretical study", *Propellants, Explosives, Pyrotechnics* **38***,* 9-13 (2013).

Jesus Paulo L. Perez, Brandon W. McMahon, Stefan Schneider, Jerry A. Boatz, Tom W. Hawkins, Parker D. McCrary, Preston A. Beasley, Steven P. Kelley, Robin D. Rogers, and Scott L. Anderson, "Exploring the structure of nitrogen-rich ionic liquids and their binding to the surface of oxide-free boron nanoparticles", *J. Phys. Chem. C*, **117**, 5693-5707 (2013).

Jesus Paulo L. Perez, Brandon W. McMahon, Jiang Yu, Stefan Schneider, Jerry A. Boatz, Tom W. Hawkins, Parker D. McCrary, Luis A. Flores, Robin D. Rogers, and Scott L. Anderson, "Boron Nanoparticles with High Hydrogen Loading: Mechanism for B-H Binding and Potential for Improved Combustibility and Specific Impulse", *ACS Applied Materials and Interfaces,* **6**,8513-8525 (2014).

Robert J. Buszek and Jerry A. Boatz, "Cage Compounds as Potential Energetic Oxidizers: A Theoretical Study of a Cage Isomer of N2O3", *Propellants, Explosives, Pyrotechnics*, 39, 787-792 (2014).

Brandon W. McMahon, Jesus Paulo L. Perez, Jiang Yu, Jerry A. Boatz, and Scott L. Anderson, "Synthesis of Nanoparticles from Malleable and Ductile Metals using Powder-Free, Reactant-Assisted Mechanical Attrition", *ACS Applied Materials and Interfaces,* **6,** 19579-19591 (2014).

S. B. Emergy, Y. Xin, C. J. Ridge, R. J. Buszek, J. A. Boatz, J. M. Boyle, B. K. Little, and C. M. Lindsay, "Unusual behavior in magnesium-copper cluster matter produced by helium droplet mediated deposition", *J. Chem. Phys*., **142**, in press.

Acknowledgements

Aluminum nanoparticles

- Prof. Scott Anderson, Brandon McMahon, Jiang Yu (Univ. of Utah)

Core-shell nanoparticles

- Dr. Robert Buszek (ERC, Inc.)
- Dr. Sam Emery(NSWC-IH), Y. Xin (Florida State Univ.), C.J. Ridge, B.K. Little, C.M. Lindsay (AFRL/RW) J.M. Boyle (Dublin School, Dublin, New Hampshire)

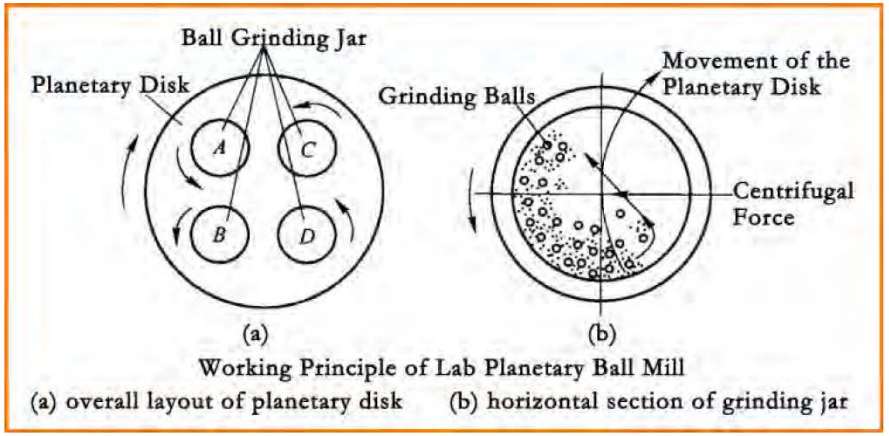
AFOSR

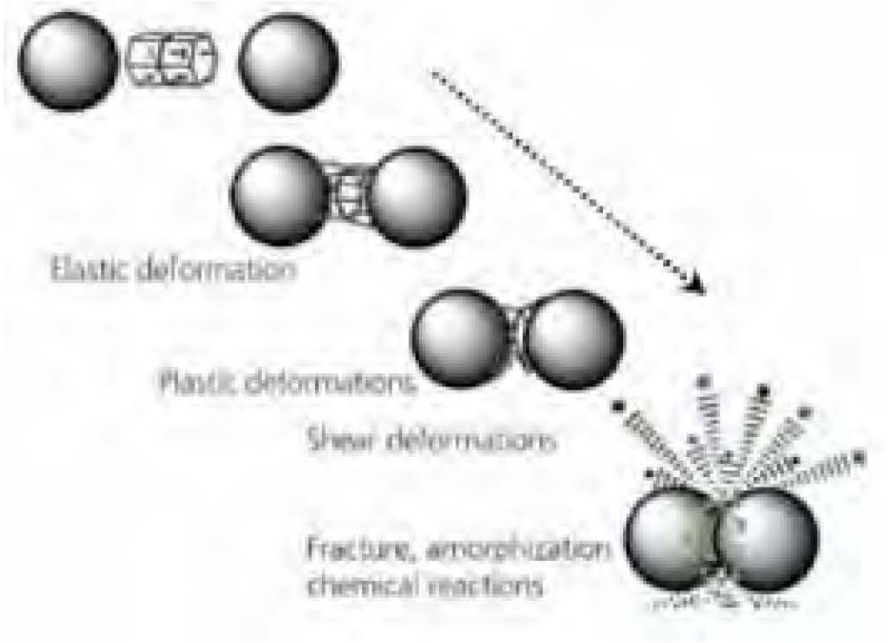
Dr. Mike Berman

DoD HPCMP

Backup Slides

Planetary ball milling





Technical Progress: EILs

- Can metal nanoclusters (e.g., aluminum or boron) form stable colloidal suspensions in ionic liquids (ILs) to produce air-stable, oxidation-resistant, hybrid fuels?
- Why do boron nanoparticles (BNPs) form stable suspensions in some solvents but not others?
- What types of chemical interactions occur between solvent/IL and BNPs?

Boron nanopowder milled in ethanol:

UNSTABLE

Boron nanoclusters precipitate out of solution.

Boron nanopowder milled in IL/ethanol mixture:

STABLE

Boron nanoclusters remain in solution; form a stable colloidal suspension

- Utilize M&S to
  - understand the difference in behavior of BNPs milled in conventional solvents vs. ILs
  - optimize the long-term stability of IL/BNP colloidal suspensions

Customers:	**RQRP / Univ. of Utah / Univ. of Alabama**
Involvement:	**experimental synthesis & data**
Sponsor:	**AFOSR**

IL/metal hybrid fuels

- Addition of 10% aluminum or boron into each bipropellant yields small changes in specific impulse for each fuel (MMH, RP1 & IL)
  - Aluminum gives slightly more positive improvement than boron
- Aluminum & Boron nano-particulate significantly increases volumetric impulse (energy density) for all 3 fuels
  - MMH/NTO does maintain Isp advantage over both hydrocarbon (RP1) and dicyanamide-based IL fuels – due to lower MW exhaust species
- Volumetric impulse of IL fuel ***without*** metal hybridization is *good*
  - Same as that of boron-bearing MMH and hydrocarbon fuels
  - Greater than aluminum-bearing MMH and hydrocarbon fuels
- IL fuel provides highest volumetric impulse of all three fuels when hybridized with metal
  - Boron & aluminum appear to provide similar predicted IL fuel performance (metal held at 10 wt% of total propellant)
  - Aluminum is more effective (i.e., lower concentration of metal required in fuel component) compared to boron to achieve same performance
    - For IL fuel, 21.7 wt% Al for 14.2 lb_f-s/in^3, versus 27.0 wt% B for same performance

IL/metal hybrid fuels

Computational model – why B_{80}??

- Calculations predict most stable forms of B_n for n < 20 are quasi-planar
- Most stable form of B_{20} is a ring

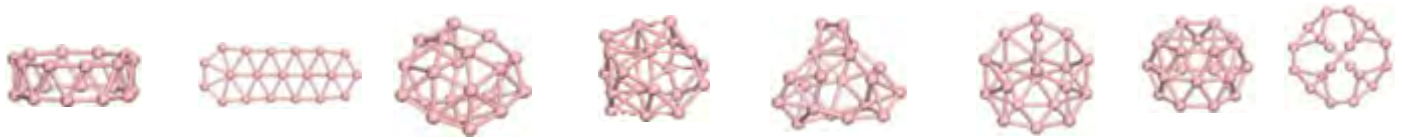


Table I. The MP2/6-311G* optimized B_{20} geometries and computed relative energies (in eV) of the eight B_{20} isomers at different theoretical levels.t1n1

Symmetry	C_{5v}	C_{2v}	C_2	C_1	C_1	C_s	C_s	S_4
CCSD(T)	0	0.72	1.46	1.87	1.97	2.31	2.80	3.45
MP2	0	1.13	1.07	0.94	1.89	1.47	1.16	3.32
PBE	0	0.67	1.51	1.69	2.26	2.52	2.60	3.80
TPSS	0	0.68	1.66	1.96	2.17	2.46	3.00	3.35
TPSSh	0	0.79	1.65	1.93	2.12	2.44	3.09	3.23
PBE0	0	0.96	1.50	1.68	2.13	2.47	2.90	3.53
mPW1PW91	0	0.99	1.75	2.15	2.37	2.74	3.74	3.75
M06-2X	0	1.11	1.03	0.93	1.61	1.98	1.13	2.71
B3LYP	0	0.99	3.25	4.24	3.82	4.39	4.80	5.34
BLYP	0	0.75	3.38	4.39	4.04	4.58	4.78	5.63

Fengyu Li, Peng Jin, De-en Jiang, Lu Wang, Shengbai B. Zhang, Jijun Zhao, and Zhongfang Chen, J. Chem. Phys. 136, 074302 (2012)

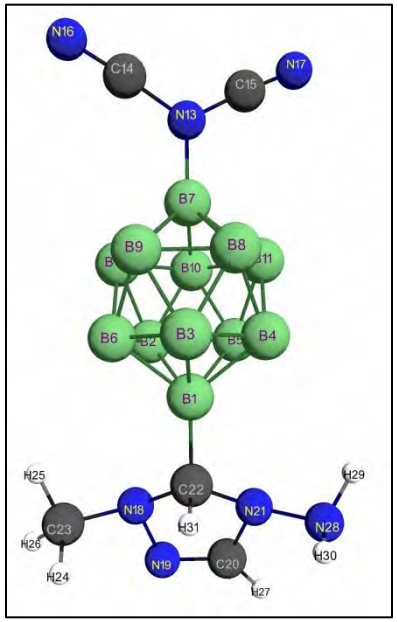
IL/metal hybrid fuels

Computational model – why B_{80}??

- IL interactions with small 3D clusters (e.g., B_{12}) inconsistent with larger clusters

B_{12} + [MAT][DCA]

E_{int} = 104.5 kcal/mol

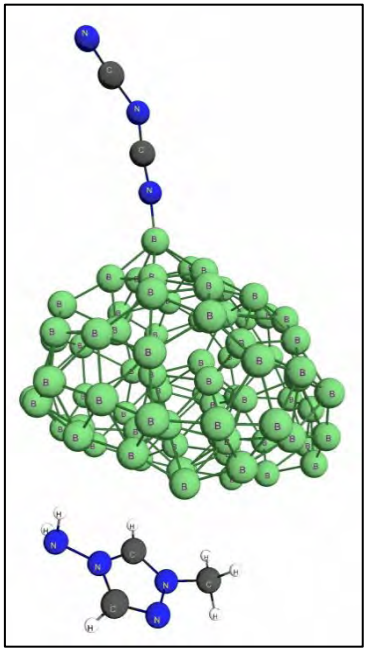


Distinct differences in

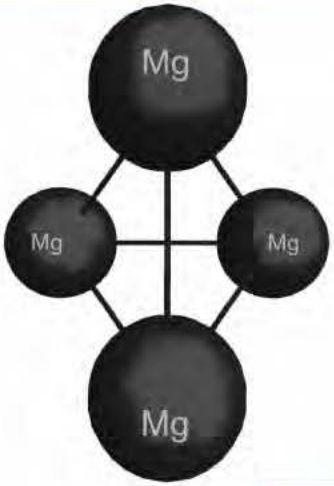
- interaction energies (2x)
- binding of cation
- binding of anion

B_{80} + [MAT][DCA]

E_{int} = 51.5 kcal/mol



Mg_n benchmark calculations



Mg_n clusters

"Closed shell" atomic configuration $[(1s)^2(2s)^2(2p)^6(3s)^2]$ suggests that weak dispersion interactions will be important. Need to consider

- core-core and core-valence correlation
- correlation method (MP2, CC, DFT)
  - "active" electrons to be correlated in MP2, CC
  - suitable DFT functional for larger Mg_n clusters (up to n ≈ 100)

Method	cc-pwCVDZ	cc-pwCVTZ	cc-pwCVQZ
MP2	23.1 / 3.042	28.5 / 3.013	29.1 / 3.011
CCSD(T)	16.7 / 3.100	tbd / 3.064	tbd / 3.065
DFT/B3PW91	26.5 / 3.092	26.5 / 3.091	26.4 / 3.092
DFT/PBE	34.6 / 3.070	34.5 / 3.070	34.3 / 3.070
DFT/PBE0	31.5 / 3.078	31.5 / 3.078	31.4 / 3.078
DFT/M06	30.8 / 3.028	30.4 / 3.025	TBD / TBD
DFT/M11	19.2 / 3.134	TBD / TBD	TBD / TBD

Calculated binding energies used to determine size of helium droplet needed for evaporative cooling